FDD FILE COPY

CLASSIFICATION [redacted]

FOR OFFICIAL USE ONLY

CENTRAL INTELLIGENCE AGENCY

INFORMATION REPORT

REPORT

STAT

COUNTRY	USSR	DATE DISTR.	13 July 1948
SUBJECT	Rare Elements	NO. OF PAGES	7
PLACE ACQUIRED	USSR	NO. OF ENCLS. (LISTED BELOW)	
DATE OF INFORMATION	1947	SUPPLEMENT TO REPORT NO.	

UNCLASSIFIED

JAN 31 1955 hm /FDD

FOR OFFICIAL USE ONLY

STAT

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE ACT 50 U. S. C., 31 AND 32, AS AMENDED. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW. REPRODUCTION OF THIS FORM IS PROHIBITED. HOWEVER INFORMATION CONTAINED IN BODY OF THE FORM MAY BE UTILIZED AS DEEMED NECESSARY BY THE RECEIVING AGENCY.

THIS IS UNEVALUATED INFORMATION FOR THE RESEARCH USE OF TRAINED INTELLIGENCE ANALYSTS

SOURCE Russian periodical, Nauka i Zhizn', No 2, 1947. (FDB Per Abs 30T57 — Translation specifically requested.)

RARE ELEMENTS IN COAL ASHES

M. A. Klochko
Doctor of Chemical Sciences

The Five-Year Plan for the restoration and development of the national economy of the USSR provides for a considerable growth in the extraction and use of rare metals. The problem of a raw material base for an industry of rare elements is especially significant in connection with this plan at the present time.

Until recently, D. I. Mendeleyev's periodic system contained 92 elements, 90 of which are found on the earth. The relative content of these elements in the obtainable parts of the earth differs greatly, especially in the separate covers of the earth -- the gaseous envelope, or atmosphere; the aqueous envelope, or hydrosphere; and the solid envelope, or lithosphere; and the area of distribution of life, which is called biosphere. The latter, embracing the entire plant and animal world of the earth, includes part of all three of the above-enumerated envelopes.

By limiting ourselves to the elements found in each of the three envelopes and in the biosphere in quantities greater than 1/100 of a percent, we obtain the following table. The elements are arranged in the order of decreasing importance for each envelope (Table 1).

CLASSIFICATION [redacted]

STATE	X	NAVY	X	NSRB		DISTRIBUTION					
ARMY	X	AIR	X	AEC	X						

[redacted]

FOR OFFICIAL USE ONLY

[redacted]

STAT

[redacted]D

Table 1. Relative Content of Elements in Different Envelopes of the Earth (According to V. I. Vernadskiy)

Envelope Content	Atmosphere	Hydrosphere	Lithosphere	Biosphere
Greater than 10%	Nitrogen, oxygen	Oxygen, hydrogen	Oxygen, silicon	Oxygen, hydrogen
Greater than 1%	Argon	Chlorine, sodium	Aluminum, iron, calcium, magnesium, sodium, potassium	Carbon
Greater than 0.1%	Hydrogen	Magnesium, sulphur	Titanium, hydrogen, carbon, phosphorous sulphur, fluorine	Silicon, potassium, calcium, nitrogen
Greater than 0.01%	Carbon	Calcium, potassium	Barium, manganese. chlorine, strontium	Sulphur, magnesium, iron, sodium, chlorine, aluminum, phosphorous

The 20 elements shown in the table comprise more than 99.9 percent of the weight of the earth's crust (all three envelopes and the biosphere). Consequently, less than 0.1 percent of the weight of the earth's crust is composed of the remaining 70 elements. At first glance such a distribution may appear strange. Actually, such well-known and sufficiently widespread metals as copper, tin, lead, zinc, nickel, mercury, and others are among these 70 elements. At the same time, we see some comparatively unknown elements, such as titanium, strontium, and argon, among the more widespread elements listed in the table. This is explained by the fact that our notion of the rarity of elements does not correspond to their relative content in the earth's crust. For example, according to various data, the little-known element, titanium, which is not widely used in technology, composes from 0.4 to 0.6 percent of the weight of the earth's crust, which is approximately 60 times more than copper, 100 times more than zinc, and 400 times more than lead. But, the last three elements are found in the form of rich sulphur deposits where they can be easily extracted; and therefore copper, zinc, and lead were long ago considered ordinary metals, while titanium, widely distributed but greatly diffused in different rocks, is considered "rare." It is clear from what has been said that it is difficult to draw an exact boundary between "rare" and "common" elements.

Many investigators refer to a major part of the elements as rare. For example, Academician A. L. Fersman proposed to consider 63 elements rare, i.e., more than two-thirds of all those discovered on the earth. Therefore, it is naturally easier to enumerate the ordinary "common" elements, which are considerably fewer in number. By adding 15 elements in the order of their degree of prevalence in nature (chromium, zirconium, vanadium, nickel, zinc, boron, copper, rubidium, lithium, cobalt, tungsten, tin, cerium, yttrium, and beryllium) to the 19 elements in Table 1 (without argon, which is considered rare), we have the 34 elements which are most

[redacted]

[redacted]

RESTRICTED

STAT

abundant in the earth's crust. However, if we compare the degree of dispersion of each element and the ease of acquiring and using it in technology, it is more correct to consider titanium, zirconium, vanadium, yttrium, tungsten, and beryllium as rare elements and to consider lead, bromine, arsenic, mercury, iodine, antimony, bismuth, and silver, which are less prevalent but better known, as ordinary elements. Thus, we have 36 elements which will be considered ordinary or common, and the remaining 54 are (naturally) rare. Elements having the most diverse properties belong to the rare group, for example: very active alkali metals -- rubidium and cesium; the so-called precious metals -- platinum, palladium; radioactive elements -- radium, thorium, uranium; and finally some rare gases -- krypton, xenon, etc. Part of the rare elements are presented below (Table 2).

Table 2

Elements	Max Content in Ashes	Avg Content in "Rich Ashes"	Avg Content in Earth's Crust	Coefficient of concentration	
	In grams per ton			Max	Avg
Boron	3,000	600	3	1,000	200
Germanium	11,000	500	7	1,600	70
Arsenic	8,000	500	5	1,600	100
Bismuth	200	20	0.2	1,000	100
Beryllium	1,000	300	5	180	50
Cobalt	1,500	300	40	35	8
Nickel	8,000	700	100	80	7
Zinc	10,000	200	40	250	5
Cadmium	50	5	0.5	100	10
Lead	1,000	100	16	60	6
Silver	5-10	2	0.1	50-100	20
Gold	0.2-0.5	-	0.005	40-100	-
Platinum	0.7	-	0.005	120	-
Lithium	500	-	65	8	-
Scandium	400	60	5	80	3-12
Gallium	400	100	15	27	7
Yttrium	800	100	31	26	3
Zirconium	5,000	-	190	26	-
Molybdenum	500	200	15	33	15
Indium	2	-	0.1	13	-
Tin	500	200	40	13	5
Thallium	5	1	0.3	17	3

Rare elements need not be confused with the so-called rare earth elements or lanthanides. Fourteen elements belong to the latter, 13 of which have been found at the present time. These have very similar chemical properties and, together with lanthanum, occupy one block in the periodic system. Oxides of these elements are called rare earths. All lanthanides are rare, although the best known of them, cerium, is more widespread than lead and bromine.

The use of rare elements in industry, medicine, and laboratories has greatly increased during the last decade. According to R. Atkinson, the production of a majority of rare elements increased several times from 1927 to 1937; for example, rhodium, 2.5 times; thorium and cobalt, four

RESTRICTED

RESTRICTED

STAT

[redacted]

times; uranium, seven times, etc. Since 1937, the production of a number of rare elements, particularly uranium, has increased still more in the USA.

The last decade before the war is characterized by increased study of the geochemistry of rare elements, i.e., the processes of their transformation, accumulation, and dispersion in the earth's crust.

Academician V. I. Vernadskiy first showed the enormous role of living organisms in geochemistry. Many elements can be accumulated in living organisms. The accumulation of potassium by some plants was used long ago as the basis for obtaining potassium carbonates, -- potash -- from the ashes of these plants. The ashes of some sea algae serve as a raw material for the extraction of iodine. It is seen from Table 1, which shows the dispersion of elements in the biosphere, that the main component parts of living organisms, including plants, are oxygen, hydrogen, and carbon. In the burning of plants those elements, together with nitrogen and to some extent sulphur, are removed. The percentage content of the residual elements in the ashes is increased several times in comparison with their content in living plants. The elementary composition of ashes of a plant depends upon its type as well as the conditions and medium in which it grew.

Undoubtedly the use of plant ashes will increase in the future, so that it will be possible not only to extract potassium compounds from these ashes, or to use them as fertilizer, but also to use them as a raw material for obtaining rare elements. It is possible that special methods of selection, sorting, growing, and cultivation of plant specimens with a maximum content of the desired element will have to be applied. The ashes which are obtained in enormous quantities in burning coal can serve as a still more important source for obtaining rare elements. These ashes have a diverse composition which is determined by all the complex and long processes of transformation of plant organisms into coal.

The content of mineral substances in various coals, and consequently their ashes, varies in very wide limits, from one to several tenths of one percent. Coal ashes may be looked upon as containing two parts: the primary, or natural, plant ash that came from the mineral substances which comprise the plant carbon-forming material; and the secondary, or external, ash of coal that is formed from mineral substances which have been carried into the coal or accumulation of plant material from outside by the wind, water currents, etc. A large part of the secondary material distributed in coal is irregular and can be mechanically separated. However, it is impossible to draw a sharp line between these two types of ashes as the composition of the ashes of the plant carbon-forming material is unknown and many mineral substances were absorbed by the coal or precipitated in it from various water currents. These substances could uniformly impregnate the entire volume of a coal bed. If the diversity in the conditions of growth of the primary plant material and its transformation into coal are taken into consideration, as well as the different compositions of the surrounding rocks, soil, and water currents which influence these processes, it can be concluded that coal ashes must contain a large number of chemical elements. Actually, in addition to the common elements of the biosphere listed in Table 1, approximately 46 rare elements are found in coal ashes.

With regard to the utilization of these ashes, various propositions for using them as raw material for obtaining aluminum salts have been made. The residue from burning coal is sometimes used as a construction material for roads, but in the main the ashes have remained unused waste. Prior to 1930, the ashes were almost never looked upon as material containing rare

[redacted]

RESTRICTED

STAT

RESTRICTED

[redacted]

elements.

In 1930, the Norwegian geochemist, V. M. Goldshmidt, published a work on the diffusion of germanium in coal and the products of its processing. Coal ashes were found to contain from 0.01 to 0.5 percent germanium. Three years later, a work by Goldshmidt and Peters on the accumulation of rare elements in coal was published. The ashes of the coal of western Germany and England were found to contain up to one percent boron, 0.1-0.2 percent cobalt, approximately 0.05 percent gallium, up to 0.1 percent beryllium, and some other rare elements. It was discovered that rare elements can accumulate in coal ashes in quantities which surpass their average content in the lithosphere. These elements are beryllium, boron, scandium, yttrium, lanthanum and lanthanides, vanadium, cobalt, nickel, molybdenum, copper, zinc, gallium, silver, platinum, palladium, and some others.

Table 2 compares the content of some elements in coal ashes with their average content in the earth's crust. It is seen from the table that the coal ashes are enriched with a number of rare elements.

The average content of some elements (boron, beryllium, cobalt, and others) reaches 100-700 grams per ton in "rich" ashes, i.e., these ashes can serve as a raw material for industrial production of such elements. Especially rich ashes contain several kilograms of germanium, arsenic, zinc, cobalt, and nickel per ton.

Under the direction of the famous English scientist, G. T. Morgan, a systematic study of coal ashes of the British Empire was made. It was found that they contained up to 1.6 percent gallium, one percent germanium, and some other elements. The precious metals, -- gold, silver, and elements of the platinum group -- were also discovered in coal ashes. V. M. Goldshmidt found silver (5-10 grams per ton), gold (0.5-1.0 grams per ton), and platinum (0.2-1 gram per ton) in some coal ashes. It is seen from Table 2 that the average coefficient of concentration of silver in coal ashes is 20, and the maximum is 50-100. The maximum coefficient of concentration of gold has the same value, and that of platinum reaches 120. There is also an indication of the presence of other platinic metals in ashes -- rhodium, rutherium, and possibly osmium. These facts are of great scientific and practical interest as they throw light on some aspects of the geochemistry of precious metals.

Approximately 60 of the 90 elements found in the earth's crust are found in living organisms and in coal ashes in almost equal amounts.

In 1934, Yo. Tilo published a complete analysis of two ash specimens: one of lower Silesian coal containing 4.3 percent ashes and the other of English coal containing 0.9 percent ashes. The results of the analyses indicate that principally oxides and then silicates and sulphates of several elements enter into the composition of ashes.

Oxides of nine elements (silicon, aluminum, iron, calcium, magnesium, sodium, titanium, and sulphur) compose 96.29 percent of the first ash specimen and 94.79 percent of the second.

Yo. Tilo determined all rare earth elements together, not distinguishing them from each other. Which of these 13 elements are found in ashes is, therefore, unknown. If we consider that only one is present in each ash specimen, then altogether 27 elements (not counting oxygen) were determined in the first specimen, and 30 in the second. The portion of 18 rare

[redacted]

RESTRICTED

STAT

elements in the ash specimen first was 3.71 percent, while the portion of oxides of 21 rare elements in the second specimen was 5.21 percent. However, it must be supposed that there was more than one lanthanide in the ash specimens, and also that others were present which were not discovered by the author. Therefore, the number of elements which he found in the ashes (27 and 30) must be considered a minimum. These ashes were strongly enriched with lanthanides (800-1,200) (numbers in parentheses indicate the content of oxide of a given element in grams of oxide per ton of ashes in the first and second ash specimens), zirconium (440-700), vanadium (1,700-700), nickel (1,400-100), cobalt, molybdenum (100-500), boron (3,000-10,000), and scandium (100).

In its formation process, coal can be enriched with any chemical element by various methods (filtration of various solutions through it, absorption and precipitation from them of various substances from these solutions). This situation can be confirmed with the application of exact methods in studying a large number of ash specimens from various coal deposits.

During recent years the study of ashes of combustible minerals and particularly coal has been widely developed in the Soviet Union.

The works of the Russian geochemists, Academicians V. I. Vernadskiy and A. Ya Fersman (and their students), gained world recognition for them. The Biogeochemical Laboratory of the Academy of Sciences of the USSR, founded in 1929 by Academician V. I. Vernadskiy and now the Laboratory of Geochemical Problems imeni V. I. Vernadskiy, is the only institution in the world that studies the regularities in distribution and laws of transformation of chemical elements in the biosphere. The processes of accumulation of rare elements in coal are studied in the Laboratory by a group of colleagues (S. A. Borovik, V. M. Ratynskiy, G. G. Bergman, and others) under the direction of Corresponding Member of the Academy of Sciences of the USSR, A. P. Vinogradov, a former student of V. I. Vernadskiy and his successor in the administration of the Laboratory. By systematic study of the so-called organogenic rock (petroleums, bitumens, mineral coals), the workers of the Laboratory discovered a considerable content of vanadium in the ashes of several petroleums and asphalts.

Coal which contained a considerable quantity of vanadium and germanium was also found. Vanadium is contained in the ashes of Chelyabinsk coal. Germanium and gallium are contained in the Khuzarin (northern Caucasus) coal. Tin was discovered in ashes of coal of the Kusnets Basin, where the concentration of tin in ashes of some beds was almost high enough for industrial purposes. This circumstance can be used to direct prospecting work for tin.

A detailed study of the distribution of germanium in coals would make it possible to explain the origin of the germanium. The accumulation of germanium in coal is explained by the fact that the germanium is taken from aqueous solutions by decomposing plant material in the process of coal formation.

In this article we have been limited to the presentation of the question of rare elements in coal ashes. However, the ashes of petroleum, peat, lignite, and other combustible minerals are of equal interest.

The study of ashes of coal and lignite, peat, slates, and petroleums undoubtedly has great prospects for us. The presence in the Soviet Union

[redacted]

STAT

of enormous supplies of combustible minerals and the increasing extraction of them guarantees large supplies of raw material in the form of ashes which contain hundreds and thousands of tons of rare and dispersed elements necessary to the national economy.

The systematic study of this type of raw material, apart from the possibility of using the valuable substances contained therein, will increase our knowledge of the behavior of various elements in the earth's crust and give a powerful impetus to the further development of biochemistry in our country.

- END -

[redacted]

[redacted]

Sanitized Copy Approved for Release 2011/06/29 : CIA-RDP80-00809A000600200147-8